Ann. Rev. Mater. Sci. 1980. 10:65–83

THE METAL-SEMICONDUCTOR INTERFACE

*8644

J. O. McCaldin[1] *and T. C. McGill*[1]
California Institute of Technology, Pasadena, California 91125

INTRODUCTION

Interfaces between metal and semiconductor may be found almost everywhere in contemporary electronics. Often the metal is there just to serve as a contact to p-n junctions in the semiconductor. At other times, the metal-semiconductor interface itself performs essential electronic functions. Considerable scientific interest has been devoted to this latter situation since early in the century, as discussed by Welker (1) in the previous volume of this series. This early work led to a rather simple and classical model, in which an electrostatic barrier ϕ arises within the semiconductor and produces the rectifying behavior. The barrier ϕ is called the Schottky barrier or Schottky-Mott barrier in remembrance of that work. The prediction of ϕ has proven not to be so simple, however, whether in terms of other phenomena (such as work functions) or in terms of fundamental theories. It is to the various contemporary aspects of this problem that the present review is principally devoted.

The most general treatments of the subject appear in the well-known 1957 book of Henisch (2) and in a more recent one by Rhoderick (3). Much of the current activity is reflected in the *Proceedings of the Annual Conferences on the Physics of Compound Semiconductor Interfaces*, usually published in the *Journal of Vacuum Science and Technology*, in addition to the standard physics journals. As for the chemical literature, there is but an occasional foray between the surface chemists and the practitioners of the metal-semiconductor interface: this in spite of the considerable emphasis on interface chemistry in recent discussions of the Schottky

[1] The support of the Army Research Office and the Office of Naval Research during the preparation of this review is gratefully acknowledged.

0084-6600/80/0801-0065$01.00

barrier. An effort is made in the present review to help bridge this gap by mention of some of the relevant accomplishments of surface chemistry.

This review consists of two parts. The first deals with various interfacial phenomena. Most fundamental among these is the interfacial energy, a thermodynamic property seldom measured in the present context. Electrostatics of the solid-vacuum interface is treated next, because it has provided so much of the data for phenomenological correlations with ϕ. The property of actual solid-solid interfaces receiving the most study today may well be structure, which we then consider. Finally, much of the current work on ϕ is treated.

The second part of the review deals with theories of the metal-semiconductor interface, most of which have tried to explain the differences in origin of the states pinning the Fermi level in the covalent materials and the lack of pinning in the more ionic materials. Many of the early theories concentrated on ideal models of the metal-semiconductor interface. However, more recently the theories have turned to the role of structure at the interface, including defects, in producing the states responsible for pinning the Fermi level.

PHENOMENA AT THE INTERFACE

Thermodynamic Properties

Thermodynamic properties are usually regarded as the most fundamental of macroscopic properties. Where surfaces are involved, and even more so interfaces, the experimental difficulties have often been prohibitive, however. This has generally been the case for semiconductors and the metal-semiconductor (M-SC) interface (4). Recently, the situation has begun to change, however, particularly as a result of careful observations made during crystal growth (5–10). Furthermore, the enormous improvements in ultra high vacuum (UHV) techniques in recent years could permit suitable control of semicondutor surfaces for thermodynamic characterization. While it is true that present UHV apparatus was developed primarily for atomistic studies of surfaces, some thermodynamic characterization could readily be accomplished in the course of operating such facilities.

First, consider what is well known about the relevant interface energies, which are perhaps better known as "surface tensions." The best characterized of these interfaces is that between liquid metal and its vapor. The free energy or surface tension, σ_{LV}, for this interface appears in several tabulations (11–13), having become rather well defined at least for the more common metallic elements. The customary units are ergs/cm^2 = mJ/m^2, and it is sometimes useful to bear in mind that

1000 mJ/m^2 typically corresponds to $\sim$0.6 eV per surface atom exposed. The magnitude of σ_{LV} is usually larger for metallic elements than other substances (13), particularly so for the transition elements. The latter have $\sigma_{LV} \gtrsim 1000$ mJ/m^2 and indeed, for the most refractory of these, $\sigma_{LV} \gtrsim 2000$ mJ/m^2. As one progresses from left to right across the periodic chart of the elements, however, σ_{LV} takes a sharp drop in the region where the common semiconductors form. This region is shown in Figure 1, and includes the elements (except for Be) that do not form compounds with Si. Figure 1 shows these elements rather arbitrarily divided into three groups: elements with high surface tension ($\sigma_{LV} >$ 600 mJ/m^2) to the left; an intermediate group ($600 > \sigma_{LV} > 300$) in the middle; elements with low surface tension to the right. The σ_{LV} values are for the liquid element near its melting point and are drawn from References 12–14 in order of descending preference. Generally σ_{LV} declines rather slowly as temperature is increased. Values for Si and Ge are not shown in the figure, because they are not known with comparable accuracy. The various data for Ge have been discussed and an average value $\sigma_{LV} = 616$ mJ/m^2 suggested (6). A value for Si of $\sigma_{LV} = 720$ mJ/m^2 has been stated without comment (10).

Surface tension between solid and vapor, σ_{SV}, is considerably harder to measure and also is subject to some well-known complications (15). The available data have been analyzed in conjunction with some empirical rules regarding heats of formation; results are tabulated for a dozen or so elements (11, 12). For each of these, σ_{SV} is larger than σ_{LV}, the excess ranging from $\sim$10–30 % of σ_{LV}. No σ_{SV} values for Si or other semiconductors appear to be reported.

Surface tension between semiconductor and metal, σ_{SL}, would be the hardest of all to measure directly. Considerable progress is being made,

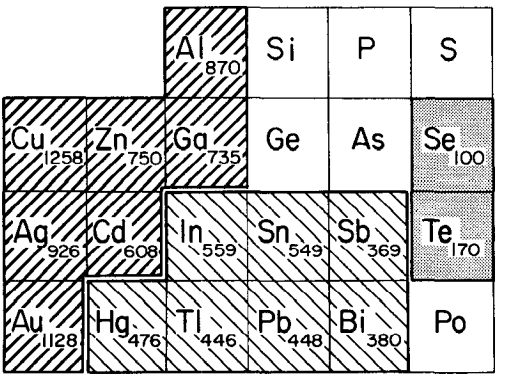

Figure 1 Surface tensions, in mJ/m^2, are shown for elements near Si in the periodic chart.

however, through contact angle measurements. The schematic of Figure 2 recalls for the reader the way in which three phases converge to form the contact angle θ. Equilibrium considerations lead to Young's equation (16)

$$\sigma_{SV} - \sigma_{SL} = \sigma_{LV} \cos \theta. \qquad 1.$$

Since σ_{LV} is relatively well known, as just discussed, measurement of θ defines the right-hand side of Equation 1. Thus one obtains a value of σ_{SL} compared to σ_{SV}, if not a value for σ_{SL} itself.

Until recently, the contact angle between a crystal and its own melt was assumed to be zero. Work by several investigators (5–10) now confirms that such is not the case for Si and Ge, where a contact angle of the order of 10° occurs. Incidentally, the old assumption that $\theta = 0$ evidently does apply to metals like Cu (7) and Ga (8). Since liquid Si and Ge are for most purposes metallic, the result $\theta \sim 10°$ may be considered the first measurement of a contact angle for a M-SC interface. Other combinations of metal and semiconductor can readily be investigated with contemporary UHV facilities. Figure 3 shows the small contact angle exhibited by In on (100) Si in experiments performed in the authors' laboratory. For comparison, the large θ for In on SiO_2 appears in the left half of the figure. The substrate, exposing SiO_2 and Si, was subjected to 2-keV Ar^+ sputtering but was not annealed, and a moderate vacuum, baseline approximately 10^{-9} Torr, obtained. When the substrate is not sputtered, but only cleaned by conventional chemical methods, a large θ develops for In on Si, similar to that for In on SiO_2 in the figure.

Such measurements for a variety of metals on the common semiconductors could provide a more direct account of the overall energy associated with the M-SC interface than is presently available. Contact angle measurements have been pursued for other substrates with some profit. A notable example is the work of Zisman (17) on low energy

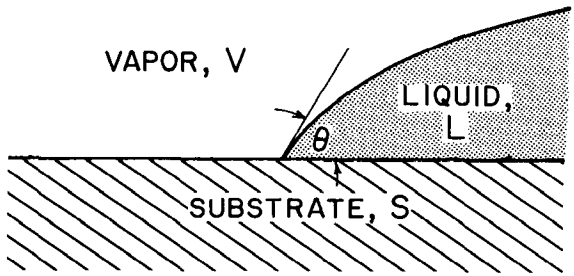

Figure 2 The contact angle θ is the arc occupied by liquid around the point of convergence of solid, liquid, and vapor.

surfaces, mostly polymers. Homologous series of organic liquids contacting a given polymer were found to exhibit a linear relation between $\cos\theta$ and σ_{LV}, thus enabling one to define a critical surface tension for each substrate corresponding to $\theta = 0°$. The critical surface tension was associated with the molecular group exposed; CF_3 endings, for example, give the lowest of all critical surface tensions, some 6 mJ/m^2. Perhaps quite a different relationship may apply to the M-SC interface.

In the absence of data on interfacial energies, resort has been made to bulk energies. The latter was invoked in various ways in correlations of Schottky-barrier heights, e.g. via the Pauling electronegativity and more directly in the work of Andrews & Phillips (18).

Work Function and Electronegativity

The original concept of the Schottky barrier invoked the work functions of the two substances constituting the interface to predict the barrier height. While this simple procedure has not in general proven sufficient, the work function, W_F, and related parameters remain of primary im-

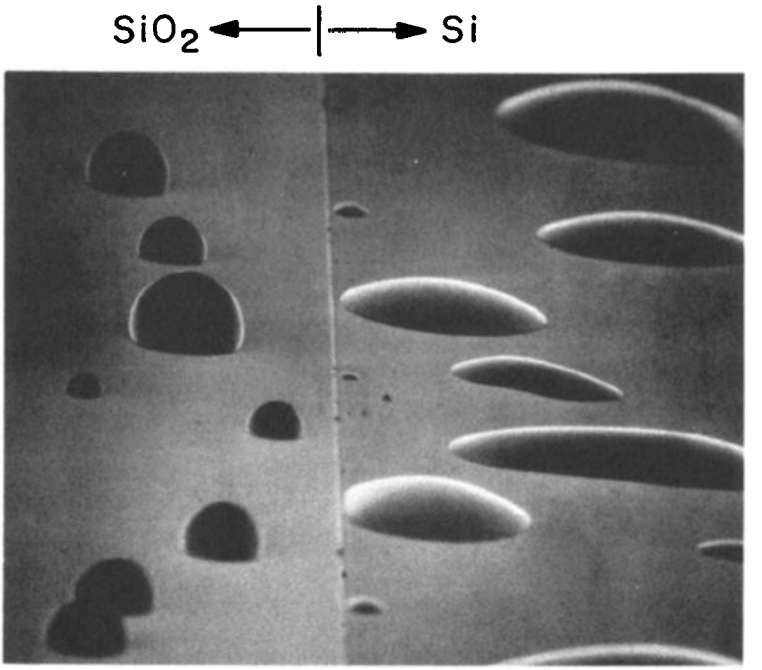

Figure 3 Scanning electron microscope view, at grazing incidence, of the configurations adopted by an In film upon melting on SiO_2 (*left*) and on Si (*right*). The largest blob on the left has a diameter of $\sim 25\ \mu m$.

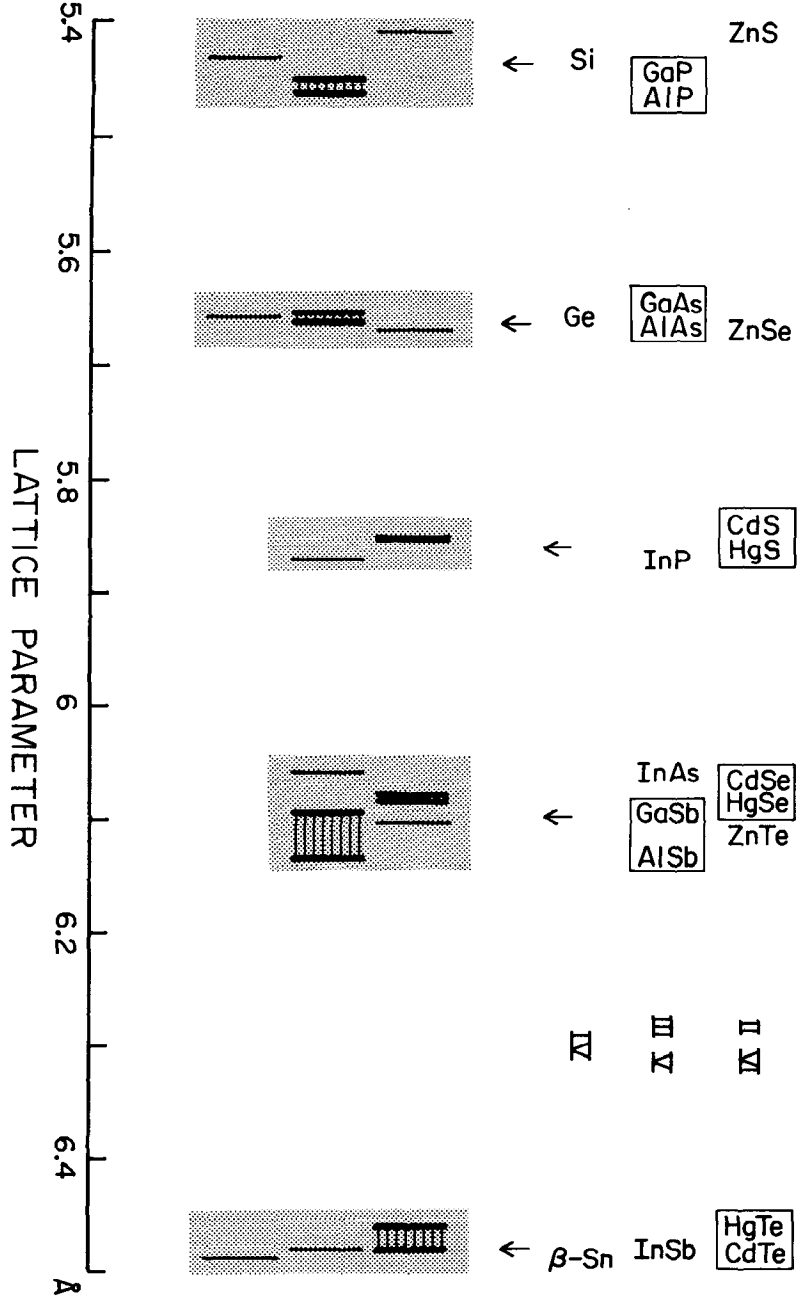

Figure 4 Lattice parameters of the common semiconductors tend to cluster. Within each cluster, lattice-matched pairs are shown in boxes.

portance in both theoretical and phenomenological treatments of the barrier. The accepted values of W_F do change with time, however. Comparison of the Michaelson compilations of W_F made in 1950 (19) and 1978 (20) indicates some shifts as large as 0.5 eV. Consequently, electronegativity, which is founded in better characterized phenomena, has often been used in place of W_F in experimental correlations of barrier height. The Pauling electronegativity has undergone some changes, however: the 1975 values (21) for six elements differ from the 1960 values (22).

Structural Properties

At first glance one might expect the semiconductor interface with vacuum to be the simplest starting place from which to view the formation of M-SC structures. In fact, however, this interface is complicated by reconstruction of the surface. For example, LEED observations show that a multiplicity of reconstructions occur on various GaAs faces (23). The determination of atom positions in such reconstructions has received much attention, but frequently presents a rather formidable problem. On (111) Si surfaces, the 2×1 structure appears to be better understood than the rather complex 7×7 structure (24–28). For (100) Si, recent results disagree with proposed geometrical models (29). In some respects the situation for GaAs, and perhaps most III-V and II-VI semiconductors, appears simpler. There is general agreement, for example, that (110) GaAs relaxes by moving surface As atoms outward and Ga inward (30). Recent work is devoted to determining the amount of the tilt angle by which As rotates outward (31).

Once metal atoms are introduced to the semiconductor surface, a number of events can occur. Perhaps the simplest is for the added atoms to continue the bulk crystal structure of the substrate, as reported for Al on GaAs (32) and Au on GaAs (33), for example. Reaction with the substrate is a further possibility, either by simple interchange (34) or perhaps involving defects. Since bonds must be broken, both temperature and structural defects (35) are likely to play a role.

In any event, one eventually lays down substantial metal upon the semiconductor and this final structure is studied in its own right. Such studies have probably proceeded furthest in the case of SC-SC interfaces, the so-called heterostructures. This work, recently reviewed by Olsen & Ettenberg (36), deals with bulk analogs of the subjects mentioned above: dislocations instead of point defects, strain instead of atom displacement, etc. In fact, it has developed to a rather sophisticated state. Quaternary systems can be laid down layer by layer in a lattice-matched condition. For the III-V materials primarily investigated in such work, it appears

that the better the lattice match, the better the electronic behavior of the interface (36).

Some of the lattice-matched heterostructures are also Schottky barriers. This comes about because the band gap, E_g, goes to zero for some compositions among the II-VI compounds, so that one side of the heterostructure approaches the behavior of a metal in a M-SC structure. The room temperature lattice parameters of the common semiconductors are displayed in Figure 4, where they can be seen to cluster in five groups. Three of these are based on the elemental semiconductors, Si, Ge, and β-Sn, and the other two are interrow combinations. Within the clusters are some closer matches whose lattice parameters are given in Table 1. Most of these close lattice matches depend on size equivalence between the cations Al-Ga and Cd-Hg. Thus, for example, AlAs-GaAs or CdSe-HgSe tend to be lattice-matched. In the latter example, the zero-gap compound HgSe occurs and thus confers on this pair characteristics of a Schottky barrier. The lattice-matched Schottky barriers CdX-HgX, where X is a chalcogen, are discussed in the section on Schottky barriers.

Electrical Properties

Electrical behavior at M-SC interfaces is dominated by the electrostatic barrier, ϕ. The way in which this barrier controls electrical properties has been discussed many times (38); here we discuss only the physical, or chemical, origin of ϕ. Only limited agreement exists today on this subject, and some investigators even feel that understanding will be attained only substance by substance: "a 'general' theoretical model valid for all the metal-semiconductor interfaces appears a more and more difficult goal . . ."

Table 1 Closely lattice-matched pairs of binary semiconductors

Semiconductor pair	Lattice parameter (Å)	Reference	Mismatch (%)
CdS	5.8503[a]	37	~0.01
β-HgS	5.851		
CdSe	6.079[a]	37	0.08
HgSe	6.084		
GaAs	5.6534	36	0.126
AlAs	5.6605		
CdTe	6.481	37	0.32
HgTe	6.460		

[a] Where hexagonal crystal structures occur, the lattice parameter quoted is for basal plane matching with the cubic structure.

(39). As for the experimental situation, the list of parameters that can affect the barrier is increasing.

With so many uncertainties attending the subject, are any generalizations possible? Probably most investigators today would still agree that barriers on semiconductors like silicon are relatively insensitive to the choice of metal, whereas the more ionic semiconductors, e.g. ZnS, show wider variation in ϕ with the choice of metal. Whether or not the transition between these behaviors is sharp, which experimental ϕ's are to be preferred, etc, are questions subject to dispute. Various aspects of the experimental definition of ϕ are treated in this section.

A fundamental problem has been present all along: Is the barrier uniquely defined by the materials forming it? Let ϕ_{MS} be the barrier between metal and semiconductor. For ϕ_{AlSi}, the widely used combination used in the integrated circuit industry [e.g. in transistor-transistor logic (TTL) "Schottkies"], a range of values has been known for many years to occur. The range can exceed one-quarter volt for common processing conditions and, indeed, various proprietary treatments have been used to stabilize ϕ_{AlSi}. In this particular example, impurities at the interface are likely involved, though this is presumably not so in other instances. The p-InP/n-CdS heterojunction, somewhat analogous to a Schottky barrier, has been prepared by the cleanest methods available today. Yet the voltage offset, in this case ΔE_c for the conduction band, depends on the preparative method selected to the extent of ~ 0.5 eV (40, 41). As we review recent Schottky-barrier measurements, it becomes evident that several parameters must be specified to fix ϕ. To illustrate the magnitude of this problem, however, we first highlight literature on interfaces that appear to exhibit no barrier.

OHMIC CONTACTS For a substance like ZnS, which has $\phi \gtrsim 0.8$ eV for all metals studied (42) and which cannot be heavily doped to induce tunneling contact, one wonders how the interior of the substance can be made accessible to electrical contact. Early work on this material obtained ohmic contact by etching in 250°C pyrophosphoric acid, followed by scribing on In amalgam and by firing in H_2 at 350°C (43). Thus the apparently high values of ϕ were circumvented. Incidentally, In amalgam scrubbed in at room temperature yields good ohmics on a wide variety of semiconductor substrates (44) for reasons not yet elucidated.

Considerably more sophisticated ohmic contacts have been prepared during the past three or four years by workers utilizing UHV with associated spectroscopies. Williams and associates in a series of investigations on InP (45–47) find $\phi = 0$ for Al, Fe, and Ni deposited on clean (110) material, whereas these same metals give $\phi \sim 0.5$ eV when deposited

on etched (110) InP. Just the opposite occurs when the metals are Ag or Au. These give a ~0.5 eV barrier when deposited on clean (110) InP at room temperature, but give ohmic contact when one-half monolayer of oxygen or chlorine is present on the InP prior to metal deposition. On the other hand, Farrow (48) and Massies et al (49) find that even Ag on clean InP gives ohmic contact provided that the crystal face exposed is (100). These results suggest that interface chemical reaction is an important consideration in InP.

The literature on ohmic contacts is extensive if one includes, as we have above, data that are incidental to the main purpose of a paper. Tabulations of various recipes have been presented by Milnes & Feucht (50), as well as Rideout (51). We have cited above only a few examples, however, to illustrate the point that low barriers are quite achievable, whether by witchcraft or the most modern scientific methods.

SCHOTTKY BARRIERS After one examines the many recipes for making low barriers, it seems rather remarkable that high barriers can be made reproducibly, as they are in industry, especially since a small area of low barrier height in parallel would effectively represent a short circuit. On the other hand, ϕ seldom rises to the height of the band bending in a p-n junction, as has become somewhat painfully clear in the photovoltaic field. Cases of maximum barrier height, $\phi \approx E_g$, where E_g is the band gap, are rare. Examples are the n-type antimonides, p-InAs (52) and p-PbTe (53), most of which have small band gaps. A more common result (54) is $\phi \approx \frac{2}{3}E_g$. Larger effective ϕ, desirable in Schottky-barrier solar cells, sometimes results from impurities deliberately introduced at the interface. Notable cases are thin oxides in Al/p-Si (55) and Au/n-GaAs cells (56).

The main new fact to emerge from the rather elegant UHV preparations of Schottky barriers during the past few years is the diversity that can be obtained. As pointed out above, ohmic contacts may be produced or not, depending on the crystal face presented by the substrate. Stoichiometry can be influential, and so can even the exact LEED pattern present on the substrate. A further important influence is temperature, which can promote interdiffusion as well as interfacial reaction, and is apt to be particularly important in the lower melting point compounds like InP. In view of this complexity, we group recent measurements of ϕ by substrate.

Silicon is still the most studied substrate if not the simplest. Roughly speaking, it remains true today that $\phi \approx \frac{2}{3}E_g$ for n-Si. The highest barrier reported (57, 58) is 0.93 eV for IrSi/n-Si, which amounts to ~0.84 E_g. The exact barrier height is of some importance in integrated circuits, where

Schottky barriers operate in conjunction with p-n junctions. Since transition metal silicide is often produced at the M-SC interface for metallurgical reasons anyway, the exact choice of transition metal can be made advantageously to fine-tune ϕ. The extensive studies of silicide-silicon systems have been reviewed by Van Gurp (59), Tu & Mayer (60), and Ottaviani (61). Also a short account appears in the book by Rhoderick (62).

Fundamental studies with Si substrates have proceeded with the full armament of spectroscopies and microscopies. Where silicide formation occurs, as just discussed, nucleation of the new phase often appears to dominate the kinetics (61), which are in any case rather complex (63). Metals that do not form bulk silicides offer a simpler prospect, although one should bear in mind that even in this case "two-dimensional" compounds may exist. For example, indirect evidence from MBE (64) suggests that such may be the case for Al on Si, and other evidence (65) indicates that an "intermediate" layer of some sort forms between Au and Si.

Extensive studies have been carried out with the non-silicide-forming metals: Al, Ga, In, Ag, and Au. A rather striking result is the insensitivity of ϕ to what occurs on the Si surface. The band bending that exists when the Si surface is bare does not change as Ag or Au is deposited (66). Neither does contamination by O_2, air, or chlorine appear to affect this result. On the other hand, Al, Ga, and In evidently introduce a shift of $\sim$0.2 eV in the band bending (39). The modification that does occur in the band bending, however, takes place for small metal coverage, of the order of a monolayer. Even though ϕ does not change much as the Si surface is metallized, the electronic states in the system change substantially. These changes have been interpreted as replacement of intrinsic surface states by extrinsic interface states, and involve formation of interface bonds followed by formation of an intermediate region between metal and semiconductor (39).

Studies utilizing III-V compound substrates encounter a rather different set of problems. Stoichiometry becomes an issue and, in practice, diffusion across the interface is often a problem. An offsetting advantage, however, is the fact, first shown clearly by van Laar (67), that the clean substrate usually has no states in the band gap, i.e. "flat band" conditions prevail near the surface. Thus the development of band bending can be followed quite sensitively as metal is deposited on the surface and appears to be completed by $\sim$0.1 monolayer coverage (35). Since these facts became evident a few years ago, a great deal of study has occurred and is only highlighted here.

GaAs has perhaps been studied the most. Conditions at the surface can be controlled very sensitively as metallization occurs. Thus single-crystal

Al can be grown on GaAs (100) to form a Schottky barrier (32). When the substrate is Ga-stabilized, ϕ is $\sim$60 meV greater than when the substrate is As-stabilized. Silver contacts on (100) GaAs have been studied in some detail and show a similar sensitivity to surface stoichiometry, as well as to impurities (49). A recent proposal ascribes the pinning of the Fermi level, as the interface is formed, to anion deficiencies (68, 69). Some support for this proposal appears to be developing at this time (1979). Thus defects of different sorts may be important in the development of the interface.

If the microscopic defects just alluded to were to become extensive enough, one would expect to detect macroscopic phenomena like diffusion. Substantial low-temperature diffusion of components of compound semiconductors reportedly occurs through Au contacts (65). The rapid degradation of ϕ for AuGe contacts on GaAs during moderate heating (70) may be related to this phenomenon. In the other direction, diffusion of Al through GaAs has been reported to be quite rapid at $\sim$850°C during LPE (71). On the other hand, interdiffusion of Al and Ga in GaAs is reportedly exceedingly slow, $D \sim 10^{-20}$ cm^2/sec, during MBE (72). Similar discrepancies are reported for Ge/GaAs interdiffusion (73, 74). The question of diffusion near interfaces is far from resolved at this time.

Similar studies on InP are in progress. Stoichiometric effects on ϕ have been found (49), and interdiffusion can clearly affect ϕ (75). As was mentioned earlier, dramatic effects on ϕ arise from the choice of crystal face on which metal is deposited. InP, if anything, appears to be richer in such phenomena than GaAs.

The investigations just discussed focus attention on the behavior of a semiconductor as metal is added, the metal coming from a rather conventional repertoire extending from Al through Au. Metals more electropositive than Al are generally too reactive to be of interest, but substances more electronegative, or "noble," than Au are potentially useful in this connection. Some of the phenomenological correlations to be discussed predict that the latter substances would give higher barriers on n-semiconductors than Au does. So far, two such substances have been investigated, polymeric sulfur nitride (76) and polyacetylene (77). Both produce high barriers; the former clearly produces higher barriers than Au.

Another approach to the attainment of higher barriers is possible with the lattice-matched Schottky barriers; CdX-HgX was mentioned in the section on structural properties. Based on W_F arguments or the "common anion" correlations discussed in the next section, one expects HgX to be effectively more electronegative than Au. Studies of CdSe-HgSe prepared by chemical vapor deposition (78) show $\phi = 0.73 \pm 0.02$ eV,

which is ~0.24 eV higher than occurs with CdSe-Au. Also noteworthy is the relatively small uncertainty in ϕ for this lattice-matched structure.

CORRELATIONS WITH OTHER PHENOMENA Accompanying the many measurements of ϕ have been attempts from time to time to find interrelations with other phenomena, either interfacial or bulk. Originally ϕ was expected to vary sensitively with W_F. In practice a smaller variation was found to occur and a correction factor S was introduced. The factor S came to be attributed to covalent or ionic character of the semiconductor side of the M-SC interface (79). Subsequently some features of this description, particularly the sharpness of the ionic-covalent transition, have been questioned (80), and agreement today is probably limited to the qualitative nature of the two regimes.

A later proposal, applicable to Au contacts on common semiconductor compounds, associated the barrier ϕ with the anion of the compound (81). This "common anion" rule met with some success in the case of ternary arsenic compounds (82), ternary phosphorus compounds (T. F. Kuech, unpublished observations), and InGaAsP quaternary compounds (83). It does not apply in other situations, e.g. to Al-containing compounds (84), where impurities are likely to occur at the interface. The proposal has been useful in suggesting means to increase barrier heights (85).

Subsequently, a scheme that classifies M-SC interfaces as reactive or nonreactive has been proposed (86). The decision as to reactivity is based on photoemission spectra, and the transition between the two classifications so far appears to be sufficiently sharp to make the distinction (87).

The correlations of most practical interest today are probably those for silicon-silicide interfaces. A proposal by Andrews & Phillips (18) based on heats of formation gave good agreement with the ϕ values then available. More recent measurements (57), however, have not conformed to the correlation. A scheme based on eutectic temperatures, however, appears to give good agreement with all the silicide barriers presently known (G. Ottaviani, unpublished data).

THEORIES OF THE SCHOTTKY BARRIER

Most of the theoretical studies of metal-semiconductor interfaces concentrate on explaining the relative independence of the barrier height on the metal in covalent semiconductors and the wide variation observed in ionic semiconductors. The theories date to the original idea of Bardeen (88) that pinning of the Fermi level on the covalent semiconductors (i.e. barrier

heights that are relatively independent of the metal) is due to the presence of surface states on the semiconductor which charge in such a way as to fix the Fermi level in the semiconductor relative to the valence band and conduction band edges. For the ionic semiconductors, only a few or no such states exist and the Fermi level is unpinned. A simple application of this concept to the electrostatics leads to a value for the slope S of the barrier height with electronegativity of the metal (89)

$$S = \frac{A}{1 + \frac{e^2}{\varepsilon_0} D(\varepsilon_F)(\delta_S + \delta_M)}, \qquad 2.$$

where A is the slope of the work function versus electronegativity of the metal, $D(\varepsilon_F)$ is the density of surface states, δ_S is the screened decay length for these states into the semiconductor, and δ_M is the Thomas Fermi screening length in the metal. Most of the theories to date are based on these ideas.

In the mid-1960s, Heine (90) pointed out that this point of view required some modification since the presence of the metal will turn most surface states on the semiconductor into states that extend throughout the metal and decay into the semiconductor. In recent years it has become clear that the states producing the pinning are not simply states that existed on the ideal semiconductor-vacuum interface. With the exception of a few of the covalent semiconductors (e.g. Si and Ge) (91, 91a,b), the ideal surface-vacuum interface of the covalent semiconductors does not possess surface states at the appropriate energy to pin the Fermi level (67, 92). Hence, the states responsible for the pinning must be due to deviations of the surface from the ideal (e.g. defects) or states introduced by the addition of the metal.

Theoretical studies (93–99) have been carried out for realistic models of the semiconductor and jellium models of the metal. The assumed semiconductor structure in these models is that obtained by simply terminating the perfect bulk. Since the metal is modeled by jellium, the interface possesses translational symmetry parallel to the interface and is much like the problem presented by a perfect semiconductor-vacuum interface. The sophistication of the calculations has ranged all the way from empirical calculations (93–95, 99) to self-consistent, pseudopotential calculations (96–98). The primary result of these calculations is the value for the density of states in the gap of the semiconductor and the appropriate decay length for these states. These parameters are then fed into Equation 2, which yields a value for S. All the theories seem to be able to explain the quantitative trend in S. That is, they find that S is typically

small for very covalent semiconductors and that S is rather large for more ionic semiconductors. The degree of agreement or disagreement depends strongly (100) on the value of A used in Equation 2. Flores et al (93–95) take $A = 1$ and claim poor agreement with experiment, while Louie et al (97) and Mele & Joannopoulos (99) use $A = 2.3$ and claim good agreement with experiment. Fits of a linear relation for the work function to the electronegativity of the metal for a recent compilation (101) of work functions suggest that A varies quite a bit for differing sets of metals. If all the metals in the compilation are used, then one obtains $A \simeq 1.8$. However, if only the metals typically used in Schottky-barrier studies are included (Al, Au, Ni, Mg, etc) (96, 96a), then a value of $A \simeq 1.0$ is obtained. This uncertainty in A, the questionable validity of the assumption that the work function of the metal is a linear function of the electronegativity of the metal, makes it difficult to decide whether or not these theories contain the major ingredients of an explanation of the Schottky-barrier phenomena.

Two of the theories disagree about whether the difference between covalent and ionic semiconductors is due to band-gap variations or due to covalency. Diamond is the important case in this discussion since diamond has a large band gap, about 5.5 eV, and yet is covalent. Mele & Joannopoulos (99) predict that diamond should have $S \approx 0$, while Ihm et al (98) predict that diamond should have $S \approx 0.4$. A very limited, old set of experimental results suggests that $S \approx 0$ (102) for diamond.

Louie and co-workers (96, 96a) calculated the value of the barrier height for Al on Si. They found that their model gives a value $\phi = 0.64$ in good agreement with the experimental value, $\phi \approx 0.75$ eV.

Inkson (103, 103a) has pointed out that the band gap of the semiconductor should be decreased at the metal-semiconductor interface as a result of the correlation between excitation in the semiconductor with the electrons in the nearby metal. In fact, he concludes that the band gap of the semiconductor may actually vanish for covalent semiconductors (typically with small band gaps). However, this effect extends only over a very small distance into the semiconductor ($\lesssim 1$ Å) and, hence, it is not at all clear that it plays an important role in determining the value of the barrier height.

More recently the theory (104, 105) has turned to trying to understand the precise role of the spatial arrangement of atoms at the metal-semiconductor interface. Mele & Joannopoulos (104) have studied the case of Al on GaAs. They conclude that in the initial stages of Al deposition on GaAs the Al replaces the surface Ga and the resulting Ga attaches to a surface As. In contrast, simple chemical considerations and quantum chemical calculations (J. J. Barton, C. A. Swarts, W. A.

Goddard, T. C. McGill, *J. Vac. Technol.* 17: In press) suggest that a single Al atom should bind to a surface Ga on a perfect GaAs (110) surface. The exchange reaction in which a surface Ga is replaced by an Al atom is exothermic but probably has a fairly substantial reaction barrier (of the order of a few eV) from the state of a Al bound to a surface Ga. These same considerations suggest that the reaction results in a Ga atom bound to the Al that has been incorporated into the GaAs (110) surface. Hence, at the present time the atomic positions for a small number of Al atoms on a perfect GaAs (110) surface is a subject of a great deal of discussion.

Following the suggestion by Spicer et al (107) that anion vacancies could be the origin of the states responsible for Fermi-level pinning on GaAs and InP, Daw & Smith (105) examined the position of the electronic levels for anion and cation vacancies as a function of spatial position from the surface. The calculations are carried out in the tight binding approximation; electron-electron interaction and lattice relaxation about the defect are neglected. They find that the position of the electronic levels of the vacancies are rather independent of the depth of the vacancy unless the vacancy is on the surface. Further, they find that in the case of both GaAs and InP the position of the Fermi level for a neutral vacancy is at the pinning position found experimentally both for metals (107) and oxides (107, 108). While these calculations for the simple vacancies may not be accurate enough to compare directly with the Fermi-level pinning position, they do suggest that defects may be the origin of the states responsible for the pinning.

In summary, a great deal of theoretical work has been directed at the metal-semiconductor interface. While this theoretical work has delineated many of the possible phenomena that can occur at the interface, we have not developed a complete microscopic picture of how important these various phenomena are in determining what occurs at a metal-semiconductor interface.

CONCLUDING REMARKS

The metal-semiconductor interface, or "Schottky barrier," in many respects resembles a p-n junction. In the latter, properties change smoothly and predictably across an interface. By contrast, the Schottky interface usually joins quite disparate substances, which makes prediction far more difficult. A principal characteristic of these structures, their barrier height, while subject to several experimental variables, can be made stable and reproducible. But what gives rise to the barrier?

Historically, correlations with other interfacial phenomena have been pursued, particularly work functions and thermodynamic properties.

The main effort to understand these structures today, however, is by direct study of the interface itself as it is being formed. Such studies are revealing in considerable detail the way interface states arise and are influencing theoretical treatments. The latter have focused on the covalent versus ionic character of the interface, but more recently are taking into account atomic arrangement at the interface and even structural defects.

Literature Cited

1. Welker, H. J. 1979. *Ann. Rev. Mater. Sci.* 9:1–21
2. Henisch, H. K. 1957. *Rectifying Semiconductor Contacts*. London: Oxford Univ. Press. 372 pp.
3. Rhoderick, E. H. 1978. *Metal-Semiconductor Contacts*. Oxford: Clarendon. 201 pp.
4. Zettlemoyer, A. C. 1969. In *Ohmic Contacts to Semiconductors*, ed. B. Schwartz, pp. 48–66. New York: The Electrochemical Society. 356 pp.
5. Antonov, P. I. 1965. *Sb. Rost Kristallov.* 6:158 [English transl: *Growth of Crystals* (Consultants Bureau, New York, 1968)]
6. Bardsley, W., Frank, F. C., Green, G. W., Hurle, D. T. J. 1974. *J. Cryst. Growth* 23:341–44
7. Wenzl, H., Fattah, A., Uelhoff, W. 1976. *J. Cryst. Growth* 36:319–22
8. Wenzl, H., Fattah, A., Gustin, D., Mihelcic, M., Uelhoff, W. 1978. *J. Cryst. Growth* 43:607–12
9. Surek, T. 1976. *Scr. Metall.* 10:425–31
10. Harrill, M. D., Rhodes, C. A., Faust, J. W. Jr., Hilborn, R. B. Jr. 1978. *J. Cryst. Growth* 44:34–44
11. Jones, H. 1971. *Met. Sci. J.* 5:15–18
12. Overbury, S. H., Bertrand, P. A., Somorjai, G. A. 1975. *Chem. Rev.* 75:547–60
13. Osipow, L. I. 1962. *Surface Chemistry*, pp. 281–92. New York: Reinhold. 473 pp.
14. Rialland, J. F., Perron, J. C., Robert, J. 1979. *Phys. Lett. A* 72:467–69
15. Herring, C. 1952. In *Structure and Properties of Solid Surfaces*, ed. R. Gomer, C. S. Smith, pp. 5–72. Chicago: Univ. Chicago Press
16. Adamson, A. W. 1976. *Physical Chemistry of Surfaces*. New York: Wiley. 698 pp. 3rd ed.
17. Zisman, W. A. 1964. In *Contact Angle, Wettability, and Adhesion*, pp. 1–51. Washington DC: American Chemical Society
18. Andrews, J. M., Phillips, J. C. 1975. *Phys. Rev. Lett.* 35:56–59
19. Michaelson, H. B. 1950. *J. Appl. Phys.* 21:536–40
20. Michaelson, H. B. 1978. *IBM J. Res. Dev.* 22:72–80
21. Pauling, L., Pauling, P. 1975. *Chemistry*, p. 175. San Francisco: Freeman. 767 pp.
22. Pauling, L. 1960. *The Nature of the Chemical Bond*, p. 93. Ithaca: Cornell Univ. Press. 644 pp. 3rd ed.
23. Cho, A. Y., Arthur, J. R. 1976. *Prog. Solid State Chem.* 10:157–91
24. Rowe, J. E., Schlüter, M., Cardillo, M., Becker, G. E. 1979. Unpublished
25. Snyder, L. C. 1979. *J. Vac. Sci. Technol.* 16:1266–69
26. Miller, D. J., Haneman, D. 1979. *J. Vac. Sci. Technol.* 16:1270–85
27. Monch, W., Feder, R., Auer, P. P. 1979. *J. Vac. Sci. Technol.* 16:1286
28. Hansson, G. V., Flodstrom, S. A. 1979. *J. Vac. Sci. Technol.* 16:1287–89
29. Himpsel, F. J., Eastman, D. E. 1979. *J. Vac. Sci. Technol.* 16:1297–99
30. Kahn, A., So, E., Mark, P., Duke, C. B., Meyer, R. J. 1978. *J. Vac. Sci. Technol.* 15:1223–28
31. Mrstik, B. J., Tong, S. Y., Van Hove, M. A. 1979. *J. Vac. Sci. Technol.* 16:1258–61
32. Cho, A. Y., Dernier, P. D. 1978. *J. Appl. Phys.* 49:3328–32
33. Vermaak, J. S., Snyman, L. W., Auret, F. D. 1977. *J. Cryst. Growth* 42:132–35
34. Bachrach, R. Z. 1978. *J. Vac. Sci. Technol.* 15:1340–43
35. Lindau, I., Chye, P. W., Garner, C. M., Pianetta, P., Su, C. Y., Spicer, W. E. 1978. *J. Vac. Sci. Technol.* 15:1332–39
36. Olsen, G. H., Ettenberg, M. 1978.

Crystal Growth, Theory and Techniques 2:1–56
37. Roth, W. L. 1967. In *Physics and Chemistry of II-VI Compounds*, ed. M. Aven, J. S. Prener, pp. 119–64. New York: Wiley. 844 pp.
38. Sze, S. M. 1969. *Physics of Semiconductor Devices*. New York: Wiley. 812 pp.
39. Margaritondo, G., Rowe, J. E., Christman, S. B. 1976. *Phys. Rev. B* 14:5396–5403
40. Shay, J. L., Wagner, S., Phillips, J. C. 1976. *Appl. Phys. Lett.* 28:31–33
41. Yoshikawa, A., Sakai, Y. 1977. *Solid State Electron.* 20:133–37 (See Figure 7)
42. Mead, C. A. 1966. *Solid State Electron.* 9:1023–33
43. Aven, M., Mead, C. A. 1965. *Appl. Phys. Lett.* 7:8–10
44. Hill, R., Richardson, D., Wilson, S. 1972. *J. Phys. D* 5:185–87
45. Williams, R. H., Varma, R. R., McKinley, A. 1977. *J. Phys. C* 10:4545–57
46. Williams, R. H., Montgomery, V., Varma, R. R. 1978. *J. Phys. C* 11:L735–38
47. Williams, R. H. 1979. *J. Vac. Sci. Technol.* 16:1418–21
48. Farrow, R. F. C. 1977. *J. Phys. D* 10: L135–38
49. Massies, J., Devoldére, P., Linh, N. T. 1978. *J. Vac. Sci. Technol.* 15:1353–57
50. Milnes, A. G., Feucht, D. L. 1972. *Heterojunctions and Metal-Semiconductor Juntions*, pp. 293–305. New York: Academic. 408 pp.
51. Rideout, V. L. 1975. *Solid State Electron.* 18:541–50
52. McCaldin, J. O., McGill, T. C., Mead, C. A. 1976. *J. Vac. Sci. Technol.* 13: 802–6 (See Figure 3)
53. Baars, J., Bassett, D., Schulz, M. 1978. *Phys. Status Solidi A* 49:483–88
54. Mead, C. A. 1966. See Ref. 42, Figure 9
55. Charlson, E. J., Lien, J. C. 1975. *J. Appl. Phys.* 46:3982–87
56. Stirn, R. J., Yeh, Y. C. M. 1975. *Appl. Phys. Lett.* 27:95–98
57. Ohdomari, I., Tu, K. N., d'Heurle, F. M., Kuan, T. S., Petersson, S. 1978. *Appl. Phys. Lett.* 33:1028–30
58. de Sousa Pires, J., Ali, P., Crowder, B., d'Heurle, F., Petersson, S., Stolt, L., Tove, P. 1979. *Appl. Phys. Lett.* 35:202–4
59. Van Gurp, G. J. 1977. In *Semiconductor Silicon 1977*, ed. H. R. Huff, E. Sirtl. pp. 342–58. Princeton: Electrochem. Soc. 1100 pp.
60. Tu, K. N., Mayer, J. W. 1978. In *Thin Films—Interdiffusion and Reactions*, ed. J. M. Poate, K. N. Tu, J. W. Mayer. pp. 359–405. New York: Wiley. 578 pp.
61. Ottaviani, G. 1979. *J. Vac. Sci. Technol.* 16:1112–19
62. Rhoderick, E. H. 1978. See Ref. 3, pp. 171–76
63. Ho, P. S., Tan, T. Y., Lewis, J. E., Rubloff, G. W. 1979. *J. Vac. Sci. Technol.* 16:1120–24
64. Becker, G. E., Bean, J. C. 1977. *J. Appl. Phys.* 48:3395–99
65. Hiraki, A., Shuto, K., Kim, S., Kammura, W., Iwami, M. 1977. *Appl. Phys. Lett.* 31:611–12
66. McKinley, A., Williams, R. H., Parke, A. W. 1979. *J. Phys. C* 12:2447–63
67. van Laar, J., Huijser, A. 1976. *J. Vac. Sci. Technol.* 13:769–72
68. Skeath, P. R., Su, C. Y., Chye, P. W., Lindau, I., Spicer, W. E. 1979. *J. Vac. Sci. Technol.* 16:1143–48
69. Deleted in proof
70. Pruniaux, B. R. 1971. *J. Appl. Phys.* 42: 3575–77
71. Small, M. B., Ghez, R., Potemski, R. M., Woodall, J. M. 1979. *Appl. Phys. Lett.* 35:209–10
72. Dingle, R. 1977. *J. Vac. Sci. Technol.* 14:1006
73. Grant, R. W., Waldrop, J. R., Kraut, E. A. 1978. *J. Vac. Sci. Technol.* 15: 1451–55
74. Bauer, R. S., McMenamin, J. C. 1978. *J. Vac. Sci. Technol.* 15:1444–49
75. Williams, R. H., Varma, R. R., McKinley, A. 1977. See Ref. 45, pp. 4554–55
76. Scranton, R. A., Best, J. S., McCaldin, J. O. 1977. *J. Vac. Sci. Technol.* 14: 930–34
77. Ozaki, M., Peebles, D. L., Weinberger, B. R., Chiang, C. K., Gau, S. C., Heeger, A. J., MacDiarmid, A. G. 1979. *Appl. Phys. Lett.* 35:83–85
78. Best, J. S., McCaldin, J. O. 1979. *J. Vac. Sci. Technol.* 16:1130–33
79. Kurtin, S., McGill, T. C., Mead, C. A. 1969. *Phys. Rev. Lett.* 22:1433–36
80. Schlüter, M. 1978. *J. Vac. Sci. Technol.* 15:1374–76
81. McCaldin, J. O., McGill, T. C., Mead, C. A. 1976. *Phys. Rev. Lett.* 36:56–58
82. Kajiyama, K., Mizushima, Y., Sakata, S. 1973. *Appl. Phys. Lett.* 23:458–59
83. Escher, J. S., James, L. W., Sankaran, R., Antypas, G. A., Moon, R. L., Bell, R. L. 1976. *J. Vac. Sci. Technol.* 13: 874–75
84. Best, J. S. 1979. *Appl. Phys. Lett.* 34: 522–24
85. Scranton, R. A., Best, J. S., McCaldin, J. O. 1977. See Ref. 76, Figure 5

86. Brillson, L. J. 1978. *J. Vac. Sci. Technol.* 15:1378–83
87. Waldrop, J. R., Grant, R. W. 1979. *Appl. Phys. Lett.* 34:630–32
88. Bardeen, J. 1947. *Phys. Rev.* 71:717–27
89. Cowley, A. M., Sze, S. M. 1965. *J. Appl. Phys.* 36:3212–20
90. Heine, V. 1965. *Phys. Rev.* 138:A1689–96
91. Eastman, D. E., Grobman, W. D. 1972. *Phys. Rev. Lett.* 28:1378–81
91a. Wagner, L. F., Spicer, W. E. 1972. *Phys. Rev. Lett.* 28:1381–84
91b. Appelbaum, J. A., Hamann, D. R. 1976. *Rev. Mod. Phys.* 48:479–96
92. Chadi, D. J. 1978. *Phys. Rev. B* 18:1800–12
93. Flores, F., Louis, E., Yndurain, F. 1973. *J. Phys. C* 6:L465–69
94. Louis, E., Yndurain, F., Flores, F. 1976. *Phys. Rev. B* 13:4408–18
95. Tejedor, C., Flores, F., Louis, E. 1977. *J. Phys. C* 10:2163–77
96. Louie, S. G., Cohen, M. L. 1975. *Phys. Rev. Lett.* 35:866–69
96a. Louie, S. G., Chelikowsky, J. R., Cohen, M. L. 1977. *Phys. Rev. B* 13:2461–69
97. Louie, S. G., Chelikowsky, J. R., Cohen, M. L. 1977. *Phys. Rev. B* 15:2154–62
98. Ihm, J., Louie, S. G., Cohen, M. L. 1978. *Phys. Rev. Lett.* 40:1208–11
99. Mele, E. J., Joannopoulos, J. D. 1978. *Phys. Rev. B* 17:1528–39
100. Flores, F., Tejedor, C., Louis, E. 1977. *Phys. Rev. B* 16:4695–97
101. Michaelson, H. B. 1977. *J. Appl. Phys.* 48:4729–33
102. Mead, C. A., McGill, T. C. 1976. *Phys. Lett. A* 58:249–51
103. Inkson, J. C. 1972. *J. Phys. C* 5:2599–2610
103a. Inkson, J. C. 1973. *J. Phys. C* 6:1350–62
104. Mele, E. J., Joannopoulos, J. D. 1979. *Phys. Rev. Lett.* 42:1094–97
105. Daw, M., Smith, D. L. 1979. *Phys. Rev. B*20:5150–56
106. Deleted in proof
107. Spicer, W. E., Chye, P. W., Skeath, P. R., Su, C. Y., Lindau, I. 1979. *J. Vac. Sci. Technol.* 16:1422–33
108. Wieder, H. H. 1978. *J. Vac. Sci. Technol.* 15:1498–1506

Annual Review of Materials Science
Volume 10, 1980

CONTENTS